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ELECTRON GROUP POLARIZABILITY AND MOLECULAR PROPERTIES OF ORGANOPHOSPHORUS COMPOUNDS

By

HENRY TOLKMITH

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Accorded an A. Cressy Morrison Award in Natural Science in 1958 by The New York Academy of Sciences

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POLARIZABILITY OF VALENCE ELECTRON GROUPS

Introduction

Physical and chemical properties of compounds are considered to be determined, to a large measure, by the characteristics of electrons occupying the highest quantum levels. In the past, systematic description of the properties of compounds has been accomplished on the basis of ionization potentials, bond data, and data of polarization as characteristics of valence electrons. Although both the permanent dipole moment and the mean polarizability are known to be important structural characteristics, relatively less attention has been given to polarizability as a property-determining factor of compounds.

It has been shown by Fajans[1] that the molar, induced polarization (molar refraction) of a given electron group varies in a well-defined manner when this group is exposed to the influence of a given positive charge, and that the change in polarization is related to the degree of polarity of the bond uniting the positive and negative particles. Similar results have been reported by Smyth,[2] whose investigations also involved organic compounds. Implicit in these findings is the fact that the mean polarizability of a given electron group varies distinctly with molecular structure. Thus, it should be possible to describe certain properties of compounds in terms of (induced) polarizability of the valence electron groups involved. It was decided to study the extent of such relationships with organophosphorus compounds because little attention has been given thus far to the theoretical aspects of this class of compound. For the purpose of a study of this kind it was first necessary to determine data of polarizability of various electron groups. These determinations were carried out on the following theoretical basis.

The total mean polarizability α of a molecule in the direction of a given field equals the sum of polarizability by distortion (induced polarizability α_i) and of polarizability of orientation α_o and is defined by the well-known Clausius-Mosotti-Debye equation

$$\alpha = \alpha_i + \alpha_o = \frac{3}{4\pi N} \cdot \frac{M}{d} \cdot \frac{\epsilon - 1}{\epsilon + 2} \tag{1}$$

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*A major part of this work, entitled BOND REFRACTION, BOND NATURE, AND STRUCTURE OF ORGANOPHOSPHORUS COMPOUNDS, was accorded an A. Cressy Morrison Award in Natural Science by The New York Academy of Sciences, on December 4, 1958.

At a sufficiently high frequency of the alternating field the molecule will no longer be able to follow the reversals of the field, and a_o becomes zero. According to Maxwell's well-known relation between dielectric constant and refractive index, $\epsilon = n^2$, the mean polarizability of a molecule is then defined by the term

$$a_i = \frac{3}{4\pi N} \cdot \frac{M}{d} \cdot \frac{n^2-1}{n^2+2} \tag{2}$$

The polarizability a_i receives contributions from atomic cores a_A, as well as from electrons a_E, and is proportional to the molar refraction R_∞. Values of R_∞ can be determined only by extrapolation of experimental values of molar refraction R_D. For many purposes it is permissible, without serious loss of accuracy, to employ values of R_D instead of values of R_∞.[1,2] Therefore,

$$a_i = a_A + a_E \approx \frac{3}{4\pi N} \cdot R_D \tag{3}$$

It has been shown by Van Vleck[3] that EQUATION 3 can be established also on the basis of quantum mechanics. In this equation, N represents the Avogadro number and R_D the molar refraction in cubic centimeters per mole for D-light. If the value of R_D is known for a given atom, ion, or molecule, the induced polarizability $a_A + a_E$ can be determined in cubic angstrom units.

Polarizability of Various Electron Groups

The molar refraction R_D of various ions was investigated by Fajans and Joos.[4] From the data reported it was possible to determine the induced polarizability of the ions involved, according to EQUATION 3. The polarizability values obtained were as given in TABLE 1. They show clearly that the induced polarizability of a nonmetal ion receives negligible contribution from the polarizability of the positive atomic core, (for example, Cl^- as compared with Cl^{+7}), and is almost identical to the polarizability of the valence electrons involved. The polarizability of the proton itself is known to have a value of zero.[1]

On the basis of the polarizability data, as given for various atomic cores in TABLE 1, it was possible to determine polarizability values of various valence electron groups from refractive data available for various groups of atoms (see TABLES 2 and 3).

For the purpose of determining data of induced polarizability for various electron groups containing valence electrons of phosphorus from the data listed in TABLES 1, 2, and 3, it was necessary to have

TABLE 1

POLARIZABILITY OF VARIOUS IONS (α_i IN A^3)

Electron group	$1s^2$		$1s^2 2s^2 2p^6$		$1s^2 2s^2 2p^6$ $3s^2 3p^6$		$1s^2 2s^2 2p^6$ $3s^2 3p^6 3d^{10}$		$1s^2 2s^2 2p^6 3s^2$ $3p^6 3d^{10} 4s^2 4p^6$	
Nucl. charge	Species	A^3	Species	A^3	Species	A^3	Species	A^3	Species	A^3
2	He	0.2								
5	B^{+3}	0.02								
6	C^{+4}	0.012	C^{-4}	31.8						
7	N^{+5}	0.008	N^{-3}	8.74						
8	O^{+6}	(0.006)	O^{-2}	2.78						
9	F^{+7}	(0.004)	F^{-}	~ 1.05						
10			Ne	0.4						
14			Si^{+4}	0.04						
15			P^{+5}	0.028						
16			S^{+6}	0.02	S^{-2}	5.95				
17			Cl^{+7}	0.016	Cl^{-}	3.61				
18					A	1.67				
34							Se^{+6}	(0.04)	Se^{-2}	6.47
35							Br^{+7}	(0.03)	Br^{-}	4.95
36									Kr	2.52

TABLE 2

POLARIZABILITY OF VALENCE ELECTRON OCTETS* (α_E IN A^3)

Octet	Species	X						References
		H		C (aliph.)		Si		
$2s^22p^6$	$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:X$			0.634	(0.65)	0.586	(0.63)	1,2,5,8
	$H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:X$	1.424	(1.43)	1.272	(1.29)	1.344	(1.39)	1,2,5,6,9
	$C:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:X$	1.272	(1.29)	1.12	(1.15)	1.242	(1.30)	2,5,6,9
	$Si:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:X$	1.344	(1.38)	1.242	(1.30)	1.334	(1.42)	2,6,9
	$\begin{matrix}H\\H\end{matrix}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}:X$	2.172	(2.18)	2.04	(2.06)	2.132	(2.18)	1,2,5,6,9
	$\begin{matrix}H\\C\end{matrix}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}:X$	2.04	(2.06)	1.918	(1.95)	2.05	(2.11)	2,5,6,8,9
	$\begin{matrix}C\\C\end{matrix}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}:X$	1.918	(1.95)	1.806	(1.85)	1.958	(2.03)	2,5,6,8,9
	$C::\overset{\cdot\cdot}{N}:X$	2.182	(2.20)	2.078	(2.11)	2.29	(2.35)	5,8,9
$3s^23p^6$	$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:X$	2.634	(2.65)	2.572	(2.60)	2.754	(2.81)	1,2,5-9
	$H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}:X$	3.77	(3.79)	3.7	(3.73)	4.3	(4.36)	2,6,9
	$C:\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}:X$	3.7	(3.73)	3.606	(3.65)	4.208	(4.28)	2,6,8,9
	$Si:\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}:X$	4.3	(4.36)	4.208	(4.28)	4.81	(4.91)	6,9
$4s^24p^6$	$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Br}}:X$	3.59	(3.62)	3.688	(3.73)	3.95	(4.02)	1,2,5-9
	$C:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Se}}:X$	4.838	(4.89)	4.676	(4.74)			2

* Data of $\alpha_i = \alpha_A + \alpha_E$ given in parentheses.

available pertinent characteristics of the positive cores of carbon, silicon, and phosphorus. The characteristics were found to be as shown in TABLE 4.

Polarizability of the $3p^3$ Electrons of Phosphorus

In the complete electron configuration of phosphorus, $1s^22s^22p^63s^23p^3$, the 5 valence electrons are represented by $3s^23p^3$. It is well known that phosphorus shows bond hybridization to a lesser extent than carbon and

TABLE 3

POLARIZABILITY OF SHARED ELECTRON PAIRS* (α_E IN A^3)

Configuration involved		$1s^1$ (H)	$2s^22p^2$		$3s^23p^2$ (Si)	$5s^25p^2$ (Sn)	References
			C (aliph.)	C (arom.)			
$1s^1$ (H)		0.825 (0.825)	0.658 (0.67)		1.225 (1.265)		1,2,5,6,8,9
$2s^22p^2$	C (aliph.)	0.658 (0.67)	0.475 (0.495)		0.918 (0.97)	(1.63)	1,2,5-9
	C (arom.)			1.051 (1.075)	1.038 (1.09)	(1.45)	5-9
$3s^23p^2$ (Si)		1.225 (1.265)	0.918 (0.97)	1.038 (1.09)	2.2 (2.28)		6,9
$5s^25p^2$ (Sn)			(1.63)	(1.45)		(4.3)	7,9

* Data of $a_i = a_A + a_E$ given in parentheses.

silicon. Although amounting to an oversimplification, it may tentatively be permissible to consider the formation of single covalent bonds as a phenomenon involving the participation of $3p^3$ electrons of phosphorus only. On the basis of such a simplified concept, it is less complicated to describe the polarizability of the $3s^23p^3$ electrons of phosphorus. Investigations carried out with this concept in mind have given sufficiently meaningful results; as these are described in subsequent sections of this paper, a more detailed approach is unnecessary at this point.

TABLE 4

CHARACTERISTICS OF C^{+4}, Si^{+4}, AND P^{+5}

Core	C^{+4}	Si^{+4}	P^{+5}	References
Nuclear charge	6	14	15	
Polarizability (a_i in Å^3)	0.012	0.04	0.028	TABLE 1
Ionic radius (in Å)	0.2	0.39	0.35 ±0.05	10
Ionizat. potential* (in ev.)	64.48	45.13	65.01	11

*Force necessary to convert atom to positive core.

Accordingly, the $3p^3$ electrons of phosphorus were considered as participating in the formation of single covalent bonds that produced a series of groupings analogous to those listed in the TABLES 2 and 3, with phosphorus in place of X. The polarizability of valence electrons of these groupings was estimated from the data of TABLES 2 and 3 with consideration of the data given in TABLE 4, according to Coulomb's law. The values obtained by this procedure were converted to data of electron group refraction, according to EQUATION 3, and checked for accuracy by computing molar refractions from them. Comparison with experimental data of molar refraction showed that minor corrections of the estimated values of electron group polarizability were necessary. The data obtained for the polarizability of electron groups, presumably containing $3p^3$ electrons of phosphorus, were as given in TABLES 5 and 6.

The values determined for a_E, as given in TABLES 5 and 6, indicate the existence of relationships between electron polarizability and interpenetration of charge densities of electrons involved in the formation of covalent bonds of the species listed. This interpenetration of charge densities depends upon the extent of overlapping of atomic orbitals and, according to the Pauling-Slater theory, determines the strength of the covalent bond involved. Therefore, it may be expected that electron polarizability and bond energy are inversely proportional. This has been found to be true and will be shown in detail below under *Bond Energy and Interatomic Distance.*

Polarizability of the $3s^2$ Electrons of Phosphorus

The availability of data of polarizability of the $3p^3$ electrons of phosphorus made it possible to determine corresponding data for electron groups involving the $3s^2$ electrons of phosphorus. This electron pair may be considered to remain unshared in compounds containing tricovalent phosphorus or to produce various coordinate bonds such as P→O, P→N, P→S, and P→Se. The polarizability of electron groups involving $3s^2$ electrons of phosphorus was determined by the following method.

From the experimentally known molar refraction R_D of a given phosphorus compound the induced polarizability a_I was calculated according to EQUATION 3. From the data given in TABLES 1, 5, and 6, the sum of polarizabilities of the atomic cores (a_A) and electron groups (a_E) of the molecule was calculated. The balance of a_I and the sum of atomic and electron group polarizabilities was taken to represent the polarizability of electron groups involving $3s^2$ electrons of phosphorus. The data obtained were as given in TABLE 7. An especially interesting result of this investigation was the determination of induced

TABLE 5

POLARIZABILITY OF ELECTRON OCTETS INVOLVING $3p^3$ ELECTRONS OF PHOSPHORUS

Octet	Species	α_E (Å^3)		α_i (Å^3)	Octet refraction*
		Estimated	Corrected		
$2s^22p^6$	$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}:\mathrm{P}$	~ 0.6	0.565	0.597	1.5
	$\mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:\mathrm{P}$	~ 1.3	1.255	1.289	3.25
	$\mathrm{C}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:\mathrm{P}$	~ 1.1	1.085	1.131	2.85
	$\mathrm{Si}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:\mathrm{P}$	~ 1.2	1.155	1.229	3.10
	$\mathrm{P}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:\mathrm{P}$	~ 1.1	1.090	1.152	2.90
	$\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}:\mathrm{P}$	~ 2.0	2.035	2.071	5.22
	$\begin{matrix}\mathrm{H}\\ \mathrm{C}\end{matrix}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}:\mathrm{P}$	~ 1.9	1.87	1.918	4.83
	$\begin{matrix}\mathrm{C}\\ \mathrm{C}\end{matrix}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}:\mathrm{P}$	~ 1.8	1.705	1.765	4.44
	$\mathrm{C}:\,:\overset{\cdot\cdot}{\mathrm{N}}:\mathrm{P}$	~ 2.2	2.20	2.248	5.65
	$\mathrm{P}:\overset{\mathrm{H}}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}}:\mathrm{P}$	~ 1.9	1.825	1.889	4.76
	$\mathrm{P}:\overset{\mathrm{C}}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}}:\mathrm{P}$	~ 1.8	1.74	1.816	4.57
$3s^23p^6$	$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:\mathrm{P}$	~ 2.7	2.725	2.759	6.95
	$\mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}:\mathrm{P}$	~ 4.3	4.33	4.378	11.05
	$\mathrm{C}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}:\mathrm{P}$	~ 4.0	4.01	4.07	10.26
	$\mathrm{Si}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}:\mathrm{P}$	~ 4.6	4.61	4.698	11.85
	$\mathrm{P}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}:\mathrm{P}$	~ 4.2	4.135	4.211	10.6
$4s^24p^6$	$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Br}}}:\mathrm{P}$	~ 3.9	4.0	4.058	10.2

*In cubic centimeters per mole for *D*-light (from α_i, according to EQUATION 3).

TABLE 6

POLARIZABILITY OF ELECTRON PAIRS INVOLVING $3p^3$ ELECTRONS OF PHOSPHORUS

Type of shared electron	Species	α_E (Å^3) Estimated	α_E (Å^3) Corrected	α_l (Å^3)	Electron pair refraction*
$1s$	H:P	~0.9	0.845	0.873	2.2
$2s^2$ or $2p^2$	C(aliph.):P	~0.7	0.695	0.735	1.85
	C(arom.):P	~1.0	1.05	1.09	2.75
$3s^2$ or $3p^2$	Si:P	~1.4	1.28	1.348	3.4
$3p^3$	P:P	~1.3	1.33	1.386	3.5

*In cubic centimeters per mole for D-light (from α_l, according to EQUATION 3).

polarizability and of refraction of an unshared pair of electrons (see fifth column of TABLE 7). Polarizability data and data of refraction pertaining exclusively to unshared electron pairs of any kind were not known previously.

TABLE 7

POLARIZABILITY OF ELECTRON GROUPS INVOLVING $3s^2$ ELECTRONS OF PHOSPHORUS

Type of compound	R_D*	α_l†	$\alpha_A + \alpha_E$†	P:	$\mathrm{P^+}{:}\underset{\cdot\cdot}{\ddot{\mathrm{O}}}{:}^-$	$\mathrm{P^+}{:}\underset{\cdot\cdot}{\ddot{\mathrm{N}}}{:}^-$	$\mathrm{P^+}{:}\underset{\cdot\cdot}{\ddot{\mathrm{S}}}{:}^-$	$\mathrm{P^+}{:}\underset{\cdot\cdot}{\ddot{\mathrm{Se}}}{:}^-$
PH_3	11.9[2]	4.72	2.62	2.10				
PCl_3	26.27[12]	10.42	8,28	2.14				
PBr_3	36.07[12]	14.30	12.17	2.13				
$P(-O-C)_3$	13.95[13,14]	5.53	3.39	2.14				
$POCl_3$	25.05[12]	9.95	8.28		1.63			
$PO(-O-C)_3$	12.70[13,14]	5.04	3.39		1.65			
$\cdot N{=}P(-O-C)_3$	14.35[15,16]	5.69	3.39			2.30		
$PSCl_3$	32.8[17]	13.02	8.28				4.74	
$PS(-O-C)_3$	20.4[13,18]	8.11	3.39				4.72	
$C_{(al.)}PSe(-O-C)_2$	23.15[19]	9.20	3.00					6.2
			Mean value of α_E†	2.13	1.64	2.30	4.73	6.2
			Electron group refraction*	5.4	4.15	5.80	11.90	15.60

*In cubic centimeters per mole for D-light.

†In Å^3.

According to the data of TABLE 7, the polarizability of a pair of unshared electrons on phosphorus $3s^2$ is not markedly influenced by the nature of the groups attached to phosphorus by its $3p^3$ electrons. The α_E values of the electron octets of the groups P→O and P→S are 0.32 and 0.29 Å^3 units higher than the respective values of electron octets of C→O and C→S. This is to be expected from the data given in TABLE 4.

The nitrogen core N^{+5} is known to have a polarizability, ionic radius, and ionization potential of 0.008 Å^3, 0.15±0.05 Å, and 113.87 ev., respectively. Upon comparison of these data with the data for P^{+5} in TABLE 4, it may be estimated that the polarizability of the unshared electron pair of nitrogen amounts to about 1.1 Å^3.

Interrelations Involving Polarizability

The polarizability data determined for various electron groups permitted studying the change of polarizability of valence electron octets of the neon ($2s^2 2p^6$), argon ($3s^2 3p^6$), and krypton ($4s^2 4p^6$) shells under the influence of the positive core of the phosphorus atom. Such changes were found to be as shown in FIGURE 1. The trend of these changes is quite similar to trends produced by positive cores of other atoms, when in place of phosphorus. Patterns of this kind were first discovered by Fajans[1] in his studies on refraction of various types of compound and led to a series of rules of ion deformation named after their discoverer.

The changes in polarizability, as illustrated in FIGURE 1, permitted estimation of the value of polarizability of the $4s^2 4p^6$ octet on selenium in the group P-Se-P. This value should equal 5.8 Å^3, and thus would correspond to a value of refraction of 14.6 cc. per mole for *D*-light. There are, at the present time, no experimental data of refraction available that would permit testing the accuracy of this value.

POLARIZABILITY AND BOND DATA

Bond Energy and Interatomic Distance

It was stated above that a mathematical relationship might be expected to exist between electron group polarizability and bond energy. Huggins[20] designated bond energies as quantities that are not strictly energies but contributions of the bonds to the heat of formation of the molecules containing them, and proved that they are computable from properly modified data of electronegativity. Huggins showed also that the interatomic distance r_{AB} can be calculated from the bond energy E_{AB} according to the equation

$$r_{AB} = r_A^* + r_B^* - 1/2 \log E_{AB} \tag{4}$$

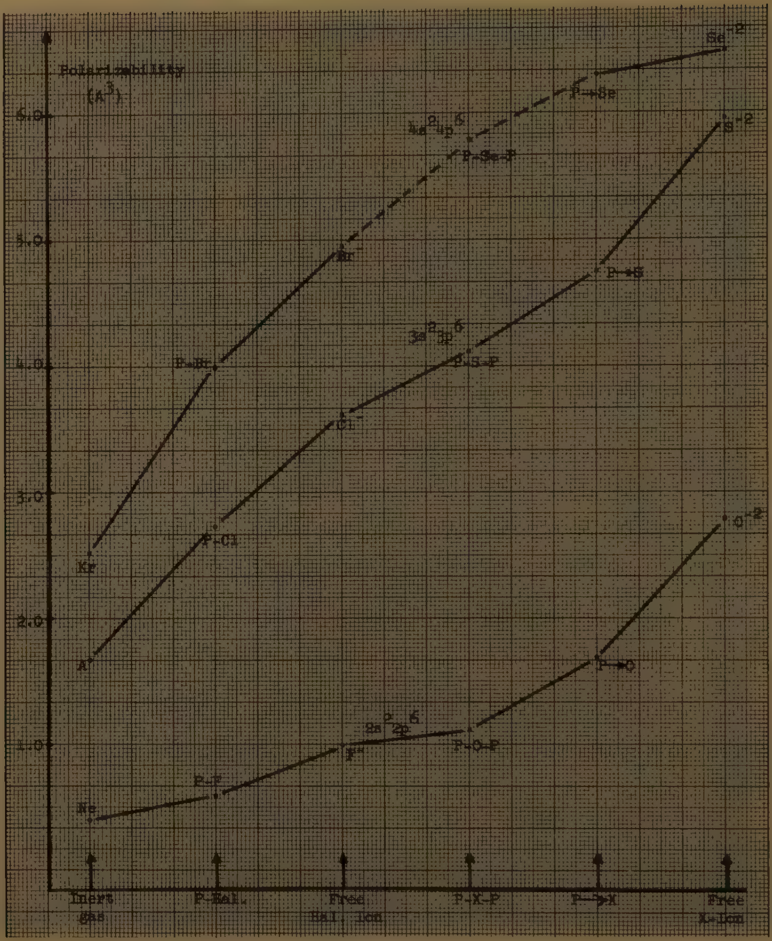


FIGURE 1. **Interrelations in polarizability of valence electron octets.**

Correlation of polarizability data, as determined for the valence electrons of phosphorus, with known data of bond energy showed existence of the relationship

$$E_{AB} = C' - C'' \cdot a_E \tag{5}$$

Combination of EQUATIONS 4 and 5 resulted in the relation

$$r_{AB} = r_A^* + r_B^* - 1/2 \log (C' - C'' \cdot a_E) \tag{6}$$

On the basis of EQUATIONS 5 and 6 it was possible to calculate bond energies and interatomic distances of phosphorus bonds from polarizability data of phosphorus valence electrons and to compare the data calculated with known data. In these calculations the following data units were employed: Data of α_E were taken from TABLES 5 and 6; the constants C' and C'' were determined separately, and C'' was found to have a constant value of 11.6 in all cases. The values of C' were found to be 110, 85, and 68 and to apply to α_E values of valence electron octets, the electron pair of P-H and of other electron pairs, respectively. Values employed for the constant energy radii $r_A{}^*$ and $r_B{}^*$, were those given by Huggins.[20] The following results were obtained:

Data of bond energy and interatomic distance, when determined by EQUATIONS 5 and 6, respectively, were found to be in satisfactory agreement with experimental data available [21,22] (TABLE 8). An exception represented the interatomic distance of the P-F bond whose calculated value was found to be in agreement with the value determined by Huggins,[20] but was not in agreement with experimental data.[22]

TABLE 8

POLARIZABILITY, BOND ENERGY, AND INTERATOMIC DISTANCE

Electron group	Bond involved	E_{AB}(Kcal./mole)		r_{AB} (A)	
		Exper.[21]	EQUAT. 5	Exper.[22]	EQUAT. 6
$2s^22p^6$	P–F		103.5	1.45 -1.59	1.63
	P–O		97 ±0.5	1.66 ±0.03	1.66
	P–N		87 ±3		1.68
$3s^23p^6$	P–Cl	78.5	78.3	2.015 ±0.015	2.02
	P–S		60.5 ±3	2.15	2.1 ±0.01
$4s^24p^6$	P–Br	63.7	63.5	2.2 ±0.04	2.19
	P–H	76.4	76.2	1.42 ±0.03	1.43
	P–C$_{(\text{al.})}$		60	1.87 ±0.02	1.86
	P–C$_{(\text{arom.})}$		55.8		1.88
	P–Si		53.15		2.24
	P–P	51.3	52.6	2.21	2.20

Bond Refraction

In analogy to the definition given for bond energy,[20] bond refraction may be considered as a contribution to molar refraction made by the electrons forming the bond involved. Some types of compounds, for example, alkanes and silanes, are composed of atoms whose cores have negligible values of refraction, and whose valence electrons are bonding electrons exclusively. The molar refraction of these compounds receives contributions only from the refraction of shared pairs of bonding electrons and, therefore, is almost equal to the sum of bond refractions. Most organic compounds, however, are composed of atoms whose valence shells contain unshared electron pairs that also contribute to refraction. The molar refraction of such compounds is larger than the sum of its bond refractions. For instance, the molar refraction of chloroform equals the sum of the refraction of one C-H bond plus the refractions of three chlorine valence octets. These octet refractions include the refraction of the C-Cl bonds; that is, the refraction of the electron pair shared by carbon and chlorine, but they also involve the refraction of the three unshared valence electron pairs of each chlorine atom. The existence of unshared electron pairs in chloroform is obscured in its valence bond structure, but is recorded in its electronic structure. Consequently, if the molar refraction of chloroform and its valence bond structure are employed to determine the bond refraction of C-Cl, the resulting value actually represents the refraction of the C-Cl bond proper plus the refraction of three unshared valence electron pairs of chlorine. A value of refraction, when determined in this manner, does not represent a bond property and should not be called a bond refraction. It actually is a refractive increment that, upon combination with other refractive increments, is supposed to produce a theoretical value of molar refraction, being practically equal to the experimental value of molar refraction of the compound involved. Thus, although the practical importance of data of refractive increments is evident, so-called bond refractions or atomic refractions derived from valence bond structures do not represent fundamental characteristics of bonds or atoms. Nevertheless, numerous data of bond refraction have been elaborated on the basis of valence bond structures (see TABLE 9).

Of the data listed in TABLE 9 those involving the bonds of hydrogen, carbon, and silicon represent quite reliable values of refractive increments that have been established by the extensive work of Vogel and his associates[8,9,12] as well as by investigations of Denbigh[5] and of Warrick.[6] Data of refractive increments involving phosphorus bonds show a less satisfactory picture. Large discrepancies exist with data pertaining to the P-H, P-C, and P=O bonds. A comparison of theoretical with experimental data of molar refraction (R_D), involving various values taken from TABLE 9, shows that the refractive constants proposed by Sayre[25] apparently are the most reliable ones.

Although the values given by Sayre[25] appear to be satisfactory, they contain a negative value of −1.032 cc. per mole for the refractive increment of the P=O bond. A similar value of −1.22 cc. per mole for this bond has recently been interpreted as lending support to the formulation of P=O as a coordinate bond.[14] However, Vogel,[8] who was

TABLE 9

KNOWN DATA OF VALENCE BOND REFRACTION (IN CUBIC CENTIMETERS PER MOLE FOR *D*-LIGHT)

Bond	X			
	H	C	Si	P
H–X	2.08[2]	1.68(±0.015)[1,2,5,8]	3.185[6,9]	2.26[23]; 4.01[25]; 4.27[24]
F–X	~1.9[2]	1.65(±0.15)[1,2,5,8]	1.6(±0.1)[6,9]	3.63[24]
Cl–X	6.675[1,2]	6.56(±0.05)[2,5,8]	7.1(±0.1)[1,2,6,9]	8.8(±0.05)[24-26]
Br–X	9.14[1,2]	9.42(±0.05)[2,5,8]	10.15 (±0.06)[2,6,9]	12.05[24]
O–X		1.5(±0.04)[5,8]	1.77(±0.03)[6,9]	3.12(±0.05)[14,23-26]
O=X		3.36(±0.05)[1,2,5,8]		+1.07(±0.15)[23,24]; −1.24(±0.02)[8,14,25]
S–X	4.8[8]	4.61[8]	6.2(±0.05)[6,9]	7.45(±0.14)[24,25]
S=X		11.26(±0.65)[2,8]		6.37(±0.07)[24,26]; 6.87[25]
N–X	1.76[8]	1.57[8]	2.16[9]	3.46[24]
C–X	1.68(±0.015)[1,2,5,8]	1.25(±0.05)[1,2,5,6,8]	2.45(±0.05)[2,6,9]	1.29[23]; 3.6(±0.02)[14,24,25]
Si–X	3.185[6,9]	2.45(±0.05)[2,6,8]	5.75(±0.1)[6,9]	5.29[24]

the first to show the existence of apparently negative values of refraction in connection with organic compounds, has stated that no explanation can be given for their negative sign.[8] Moreover, many years before these statements about the refraction of the P=O bond were published Smyth[2] had called attention to the fact that negative values for refractive increments of any group are untenable on theoretical grounds. Such negative values indicate a faulty theoretical concept employed in connection with their determination. Positive values of refraction for the P=O bond, as reported by Keeber and Post[23] and by Feher[24] nevertheless do not give agreement of theoretical and experimental R_D values (see TABLES 9 and 10).

In view of this situation it appeared desirable to attempt to establish a set of data for refractive increments pertaining to phosphorus bonds on the basis of the complete valence electron structure of phosphorus compounds. The data of refraction of various electron groups containing valence electrons of phosphorus, as given in the TABLES 5, 6, and 7, were obtained on the basis of the complete valence electron structure of phosphorus compounds, and thus appeared suitable for determination of refractive increments pertaining to phosphorus bonds. The data of refraction given in TABLES 6 and 7 were considered to be directly applicable. For some of the data of refraction, as listed in TABLE 5, it was necessary to subtract known and well-established bond refraction data[8] in order to obtain data of refractive increments pertaining to the phosphorus bond involved. The data of TABLE 11 were obtained in this manner. They might be referred to by the customary but ambiguous term of bond refraction, although they actually are refractive increments characteristic of the electron group involved.

Of the various conclusions that can be drawn from the data of TABLE 11, the following are of importance.

The so-called bond refraction of the P-O, P-S, P-N, and P-C bond is not a structure-independent constant, as implied by previously reported data (see TABLE 9), but varies with the nature of other groups, besides phosphorus, attached to O, S, N, and C of these bonds. The degree of variation in the refraction of a given covalent bond P-X in the linkage P-X-Y is moderate if X is strongly electronegative, for example, if X is oxygen, and more pronounced if X is less electronegative, for example, if X is sulfur or carbon. Relationships of this kind are to be expected from the viewpoint of electronic theory of structure and are likely to hold for the P-Si-Y linkage also.

The refractive increment of the P=O bond is smaller by 1.25 units than the refractive increment of the unshared electron pair on phosphorus. Whenever valence bond structures of phosphorus compounds are employed it is necessary to consider the refraction of this electron pair to be

TABLE 10

ACCURACY OF REPORTED REFRACTIVE INCREMENTS OF VALENCE BONDS OF PHOSPHORUS (IN CUBIC CENTIMETERS PER MOLE FOR *D*-LIGHT)

	R_D Calculated			R_D Experim.	
	Keeber[23]	Feher[24]	Sayre[25]	Reported	Reference
$(C_2H_5O)_3PO$	43.56	44.11	41.80	41.87	13
$(C_2H_5)_2PO(OC_2H_5)$	37.06	42.15	39.75	39.27	27
$C_2H_5PO(H)(OC_2H_5)$	28.35	33.10	30.51	30.52	27
$C_6H_5PO(H)(OC_2H_5)$	43.20	47.95	45.35	46.04	28
$Cl_2C{=}CHOPO(OCH_3)_2$	43.45	44.0	41.70	42.07	29

TABLE 11

REFRACTIVE INCREMENTS PERTAINING TO PHOSPHORUS BONDS (IN CUBIC CENTIMETERS PER MOLE FOR *D*-LIGHT)

Bond involved	Refractive increment
P-hydrogen	2.2(P–H)
P-halogen	1.5(P–F), 6.95(P–Cl), 10.2(P–Br)
P-oxygen	4.15(P=O), 1.45(P–OH), 1.35(in P–OC, P–OSi), 1.45(in P–OP)
P-sulfur	11.90(P=S), 6.25(in P–SH), 5.65(in P–SC, P–SSi), 5.3(in P–SP)
P-selenium	15.60(P=Se), 7.3(in P–SeP)
P-nitrogen	5.80(P=N), 1.7(in P–NH_2), 1.5(in P–NHC), 1.3(in $P{-}N\begin{smallmatrix}\diagup C\\ \diagdown C\end{smallmatrix}$), 1.9(in P–N=C), 1.5(in P–N–P)
P-carbon	1.85(P–$C_{aliph.}$), 2.75(P–$C_{arom.}$), 2.55(in $P{-}C{\vdots}N$), 2.7(in P–CCl_3), 2.05(in $P{-}\underset{\overset{\|}{O}}{C}$)
P-silicon	3.4(P–Si)
P-phosphorus	3.5(P–P)
(none)	5.40 (for unshared electron pair on phosphorus)

zero. This assumption results in a value of −1.25 units of refraction for the P=O bond. In accordance with Smyth's[2] early statement about theoretically meaningless negative values of refraction, a negative value of refraction for the P=O bond merely shows that an investigation of refractive properties of phosphorus bonds on the basis of valence bond structure produces fallacious results.

However, the data of TABLE 11 and the conclusions drawn from them can be considered valid only if the values given for refractive increments pertaining to phosphorus bonds are in agreement with experimental facts. Such agreement was found to exist, as will now be described.

POLARIZABILITY AND MOLECULAR DATA

Molar Refraction

The molar refraction of organic compounds is known to be a constitutive property that is essentially additive; therefore the molar refraction of organophosphorus compounds may be considered to be the sum of refractive contributions, coming from the "peripheral organic" parts of a given structure and a refractive contribution made by the "central inorganic" group built around the phosphorus atom. For example, the molar refraction of trimethyl phosphate $(CH_3O)_3PO$ may be regarded as the sum of refractive contributions of nine peripheral C-H groups and one central $(C\text{-}O)_3PO$ group. The refraction of various central groups in phosphorus compounds can be determined theoretically as well as empirically and the extent of agreement found is a criterion of the accuracy of the theoretically established data. Satisfactory agreement of data would also show the extent of strict additivity of molar refraction of organophosphorus compounds.

Theoretical determination of data of refraction of various central groups containing phosphorus atoms involves summation of values of refraction of electron groups containing valence electrons of phosphorus. Values of this kind have been listed in the TABLES 5, 6, and 7. Another theoretical method of determination of data of group refraction would involve the summation of bond refraction data (compare TABLE 11). Both methods produce the same theoretical values of group refraction.

The empirical method of determination of data of group refraction requires availability of experimental data of refraction, based upon the well-known Lorentz-Lorenz equation

$$R_D = \frac{M}{d} \cdot \frac{n^2-1}{n^2+2} \qquad (7)$$

Subtraction of refractive data of the "peripheral organic" parts from values of R_D leaves data of refraction of the central, phosphorus-containing group. Refractive data of various organic structures, as necessary for this operation, have become available by the extensive work of Vogel and his associates.[8] An example of theoretical and experimental determination of data of group refraction is given in TABLE 12.

According to the method described, the refractive data of phosphorus-containing groups (*GR*) of more than 600 organic compounds were determined theoretically and experimentally. The results obtained were as given in TABLES 13 to 17.

In the preceding tables certain compounds were listed for which no pertinent physical data were available in the literature. These compounds, originally prepared in connection with other investigations, had refractive data as given in TABLE 18.

TABLE 12

EXAMPLE OF DETERMINATION OF P-GROUP REFRACTION, GR
[EXAMPLE: $(CH_3O)_3PO$]

Theoretical ($GR_{th.}$)	Empirical ($GR_{exp.}$)
Three C—O—P groups → 8.55 (see TABLE 5)	R_D of $(CH_3O)_3PO$ → 27.8 ± 0.06[13,77]
One P=O group → 4.15 (see TABLE 7)	Nine C—H groups → 15.08[8]
Refraction of $(C—O)_3PO$ → 12.7	Refraction of $(C—O)_3PO$ → 12.72

Heterocyclic rings. These rings are known to show certain deviations in their refractive properties, customarily referred to as either optical exaltation or optical depression. When refractive properties of heterorings were first investigated it was concluded by Brühl[117] that the phenomenon of optical depression existed with unsaturated ring structures only. Many years later it was discovered by Vogel and his associates[8] that saturated ring systems may show either exaltation or depression in their optical properties and that the nature of such refractive deviation depended merely upon the size of the ring involved. Moreover, Johnson[118] found that optical depression of an unsaturated heteroring may change to optical exaltation upon proper ring substitution. It is now generally accepted that optical exaltation of ring struc-

TABLE 13

REFRACTION OF GROUPS CONTAINING TRICOVALENT PHOSPHORUS
(GR IN CUBIC CENTIMETERS PER MOLE FOR *D*-LIGHT)

Group*	GR		Ref.	Group*	GR		Ref.
	Theor.	Experim.			Theor.	Experim.	
C_x-PH_2	11.65	11.7±0.1	30	C_x-PCl_2	21.15	21.15±0.2	42
$(C_x)_2PH$	11.3	11.4	30	C_y-PCl_2	22.05	22.2±0.2	13,43
$(C_x)_3P$	10.95	10.96±0.1	13,30	$(C_y)_2PCl$	17.85	17.82	44
$(C_x)_2P-C_y$	11.85	11.85±0.27	13,31	$C-O-PCl_2$	22.15	22.15±0.1	13,26,31,36
$(C_y)_2P-C_x$	12.75	12.55±0.2	32	$(C-O)_2PCl$	18.05	18.0±0.1	13,36,39
$(C_x)_2P-O-C$	11.95	11.95±0.03	33	$C_yNH-P(O-C)_2$	17.11	17.6±0.05	45
$(C_y)_2P-O-C$	13.75	13.6±0.5	32	$(C_x)_2N-P(O-C)_2$	15.54	15.7±0.1	46,47
$(C_y)_2P-S-C$	21.16	20.93	32	$(C_x)_2N-P(C_x)(O-C)$	14.54	14.55±0.3	48
$C_x-P(O-C)_2$	12.95	12.77±0.18	19,27	$(C_x)_2N-PCl_2$	23.74	23.7	48
$C_y-P(O-C)_2$	13.85	13.95±0.1	34,35	$\begin{matrix}C_x\\C_y\end{matrix}\!>N-P(O-C)_2$	16.72	17.0±0.1	45
$(C-O)_3P$	13.95	13.91±0.2	13,36-40				
$(C-\dot{S})_2P-O-C$	28.77	28.55	41				

*C denotes aliphatic or aromatic carbon; C_x, aliphatic carbon only; C_y, aromatic carbon only.

TABLE 14

REFRACTION OF PHOSPHORYL GROUPS (GR IN CUBIC CENTIMETERS PER MOLE FOR *D*-LIGHT)

Group*	GR			Group*	GR		
	Theor.	Experim.	Ref.		Theor.	Experim.	Ref.
$\begin{matrix}H\\C_x\end{matrix}\!>\!P(O)(O{-}C)$	11.05	11.25 ±0.15	27	$HO{-}P(O)(O{-}C)_2$	13.10	13.15 ±0.1	18
$\begin{matrix}H\\C_y\end{matrix}\!>\!P(O)(O{-}C)$	11.95	11.95 ±0.1	28	$(C{-}O)_3P(O)$	12.70	12.7 ±0.1	13,29,57,75-77
$(C_x)_2P(O)(O{-}C)$	10.70	10.6 ±0.2	27,49,50-54	$Si{-}O{-}P(O)(O{-}C)_2$	12.95	12.95 ±0.2	74
$\begin{matrix}C_x\\C_y\end{matrix}\!>\!P(O)(O{-}C)$	11.60	11.45 ±0.15	49,54,55	$(Si{-}O)_2P(O)(O{-}C)$	13.20	13 ±0.15	23,74
$H{-}P(O)(O{-}C)_2$	12.05	12.2 ±0.15	39,56-58	$(C_x)_2P(O)Cl$	14.80	14.77 ±0.1	51,78,79
$C_x{-}P(O)(OH)(O{-}C)$	12.10	12.05	59	$C_x{-}P(O)Cl_2$	19.90	20.1 ±0.2	44,79-82
$C_x{-}P(O)(O{-}C)_2$	11.70	11.77 ±0.3	13,23,60-67	$C_x{-}P(O)(Cl)(O{-}C)$	15.80	15.8 ±0.2	36,59,64
$C_y{-}P(O)(O{-}C)_2$	12.60	12.6 ±0.07	62,68	$C_x{-}P(O)(F)(O{-}C)$	10.35	10.6 ±0.15	83
$Cl_3C{-}P(O)(C_x)(O{-}C)$	31.08	31.18 ±0.05	27	$C{-}O{-}P(O)Cl_2$	20.90	21.1 ±0.2	44,70,84,85
$Cl_3C{-}P(O)(O{-}C)_2$	32.08	32.1 ±0.1	69	$(C{-}O)_2P(O)Cl$	16.80	17.1 ±0.3	36,44,70,80
$N{\vdots}C{-}P(O)(O{-}C)_2$	17.22	17.28	70	$(C{-}O)_2P(O)F$	11.35	11.5 ±0.1	83,86
$O{=}\dot{C}{-}P(O)(O{-}C)_2$	15.22	15.2 ±0.1	27,71-72				
$Si{-}P(O)(O{-}C)_2$	13.25	13.3 ±0.15	23,74				

*Compare TABLE 13.

TABLE 15

REFRACTION OF GROUPS CONTAINING P–SULFUR AND P–SELENIUM BONDS
(GR IN CUBIC CENTIMETERS PER MOLE FOR *D*-LIGHT)

Group*	GR		
	Theor.	Experim.	Ref.
$C_x{-}P(S)(C_y)_2$	19.25	19.35	32
$(C_y)_2P(S)(O{-}C)$	20.25	20.4 ± 0.15	32
$H{-}P(S)(O{-}C)_2$	19.80	19.8 ± 0.15	87,88
$H{-}P(Se)(O{-}C)_2$	23.50	23.65	89
$C_x{-}P(S)(O{-}C)_2$	19.45	19.5 ± 0.2	19,27,54,78,90-92
$C_x{-}P(S)(OH)(O{-}C)$	19.85	20 ± 0.1	93
$O{=}\overset{|}{C}{-}P(S)(O{-}C)_2$	22.97	22.75	73
$C_x{-}P(Se)(O{-}C)_2$	23.15	23.15 ± 0.2	19,51,78,89
$C_y{-}P(S)(O{-}C)_2$	20.35	20.46	57
$C_x{-}P(S)(Cl)(O{-}C)$	23.55	23.65 ± 0.2	51,64
$C_y{-}P(S)Cl_2$	28.55	28.6	44
$HO{-}P(S)(O{-}C)_2$	20.85	20.95 ± 0.1	18
$(C{-}O)_3P(S)$	20.40	20.4 ± 0.15	13,18,40,94-97
$Si{-}O{-}P(S)(O{-}C)_2$	20.70	20.75	24
$(Si{-}O)_2P(S)(O{-}C)$	20.95	20.95 ± 0.1	24
$(C{-}O)_2P(S)F$	19.10	18.95	98
$(C{-}O)_2P(S)Cl$	24.55	24.6 ± 0.2	44,87,92,99
$(C{-}O)_2P(Se)Cl$	28.75	28.45	89
$C{-}OP(S)Cl_2$	28.65	28.7 ± 0.2	26
$HS{-}P(S)(O{-}C)_2$	28.65	28.65 ± 0.3	92,100
$C{-}S{-}P(S)(O{-}C)_2$	27.86	27.85 ± 0.4	87,96,101,102
$Si{-}S{-}P(S)(O{-}C)_2$	29.45	29.4 ± 0.05	24
$C{-}S{-}P(O)(C_x)(O{-}C)$	19.11	19.1 ± 0.15	40,91
$C{-}S{-}P(O)(O{-}C)_2$	20.11	20.1 ± 0.3	18,40,94
$(C{-}S)_2P(O)Cl$	31.62	31.85	103

*Compare TABLE 13.

TABLE 16

REFRACTION OF GROUPS CONTAINING P-NITROGEN BONDS (GR IN CUBIC CENTIMETERS PER MOLE FOR D-LIGHT)

Group*	GR Theor.	GR Experim.	GR Ref.
$H_2N-P(S)(O-C)_2$	22.82	22.75 ±0.1	104
$C_xNH-P(O)(C_x)_2$	12.68	12.35 ±0.1	51
$C_xNH-P(O)(C_x)(O-C)$	13.68	13.7 ±0.5	64
$C_xNH-P(O)(O-C)_2$	14.68	14.63 ±0.1	46,105
$C_xNH-P(S)(O-C)_2$	22.43	22.4	105
$C_xNH-P(O)Cl_2$	22.88	22.85	44
$C_yNH-P(S)(O-C)_2$	23.61	23.7 ±0.2	45
$SiNH-P(S)(O-C)_2$	22.96	23.1	24
$N{\cdot}NH-P(S)(O-C)_2$	22.85	22.85 ±0.15	44
$(C_x)_2N-P(O)(C_x)_2$	12.29	12.2 ±0.1	51
$(C_x)_2N-P(O)(C_x)(O-C)$	13.29	13.2 ±0.3	64
$(C_x)_2N-P(S)(C_x)(O-C)$	21.04	20.8 ±0.1	48
$(C_x)_2N-P(S)(O-C)_2$	22.04	21.95 ±0.1	47,104
$(C_x)_2N-P(O)(O-C)_2$	14.29	14.45 ±0.6	44,46,105,106
$(C_x)_2N-P(O)(CN)(O-C)$	18.51	18.65 ±0.15	70
$(C_x)_2N-P(O)(Cl)(C_x)$	17,39	17.24 ±0.1	44,64
$(C_x)_2N-P(O)(Cl)(O-C)$	18.39	18.32	70,106
$(C_x)_2N-P(O)Cl_2$	22.49	22.85 ±0.2	44
$(C_x)_2N-P(S)Cl_2$	30.24	30.6	47
$\begin{smallmatrix}C_x\\C_y\end{smallmatrix}{>}N-P(O)(O-C)_2$	15.47	15.1 ±0.15	15,105
$\begin{smallmatrix}C_x\\Cl\end{smallmatrix}{>}N-P(O)(O-C)_2$	19.52	19.5 ±0.1	46
$[(C_x)_2N]_2P(O)(C_x)$	14.88	15 ±0.2	107
$[(C_x)_2N]_2P(O)(O-C)$	15.88	15.87	44
$[(C_x)_2N]_2P(O)F$	14.53	15.0	70
$[(C_x)_2N]_2P(O)Cl$	19.98	19.92	106
$[(C_x)_2N]_3P(O)$	17.47	17.55	106
$O{=}C{=}N-P(O)Cl_2$	27.02	26.9	108
$SCN-P(S)(O-C)N(C_x)_2$	36.75	36.8 ±0.05	109
$SCN-P(S)[N(C_x)_2]_2$	38.34	38.87	109
$C_yN{=}P(C_x)(O-C)_2$	16.10	16.4	45
$C_yN{=}P(O-C)_3$	17.10	16.95 ±0.3	15
$N{\cdot}N{=}P(O-C)_3$	16.34	16.47 ±0.2	16

*Compare TABLE 13.

TABLE 17

REFRACTION OF POLYPHOSPHORUS GROUPS (GR IN CUBIC CENTIMETERS PER MOLE FOR D-LIGHT)

Group	GR		
	Theor.	Experim.	Ref.
$(C-O)_2P(O)-P(O)(O-C)_2$	23.2	23.25	110
$(C-O)_2P(O)-C-P(O)(O-C)_2$	23.4	23.1	111
$(C-O)_2P(O)-(C)_5-P(O)(O-C)_2$	28.58	28.57	111
$(C_x)_2P(O)-O-P(O)(C_x)_2$	18.6	18.5	50
$(C_x)(C-O)P(O)-O-P(O)(C_x)(O-C)$	20.6	20.9	64
$(C-O)_2P-O-P(O-C)_2$	25.1	25.0	13
$(C-O)_2P(O)-O-P(O)(O-C)_2$	22.60	22.5 ±0.1	68,112
$(C-O)_2P(S)-O-P(S)(O-C)_2$	38.10	37.9 ±0.1	113,114
$[(C_x)_2N](C-O)P(O)-O-P(O)(O-C)[N(C_x)_2]$	25.78	26.18	106
$[(C_x)_2N]_2P(O)-O-P(O)(O-C)_2$	25.78	25.62	106
$[(C_x)_2N]_2P(S)-O-P(S)(O-C)_2$	41.28	41.81	112
$[(C_x)_2N]_2P(O)-O-P(O)(O-C)[N(C_x)_2]$	27.37	27.84	106
$\{[(C_x)_2N]_2P(O)-\}_2O$	28.96	29.05	106
$\{[(C_x)_2N]_2P(O)-O-\}_2P(O)[N(C_x)_2]$	40.45	40.65 ±0.1	106
$\{[(C_x)_2N]_2P(O)-O-P(O)[N(C_x)_2]\}_2O$	51.94	51.2	106
$\{[(C_x)_2N]_2P(O)-O-\}_3P(O)$	51.94	51.27	106
$(C-O)_2P(O)-S-P(O)(O-C)_2$	30.3	30.3 ±0.3	115
$(C-O)_2P-N(C_x)-P(O)(O-C)_2$	25.52	25.22	116
$(C-O)_2P(O)-N(C_x)-P(O)(C_x)(O-C)$	23.27	23.22	116
$[(C-O)_2P(O)-]_2N(C_x)$	24.27	23.94	116
$[(C-O)_2P(S)-]_2N(C_x)$	39.77	39.85	116
$\{[(C_x)_2N](C-O)P(O)-\}_2N(C_x)$	27.45	27.23	116

TABLE 18

MISCELLANEOUS COMPOUNDS

Compound	M.P. (C.°)	B.P. (C.°/10 mm.)	d_4	n_d	R_D found
CH_3POCl_2	33	53 to 54	1.4382 (40°)	1.4526 (40°)	24.96
$(C_4H_9O)_2POCl$		129 to 30	1.0772 (20°)	1.4306 (20°)	54.90
$CH_3NHPSCl_2$		87 to 88	1.4694 (20°)	1.5609 (20°)	36.14
$(CH_3)_2NPOCl_2$		73 to 74	1.3500 (20°)	1.4640 (20°)	33.11
$C_2H_5NHPOCl_2$		121 to 122	1.3873 (20°)	1.4694 (20°)	32.54
$C_2H_5NHPSCl_2$		98 to 99	1.3803 (20°)	1.5452 (20°)	40.79
$(C_2H_5)_2NPOCl_2$		92 to 93	1.2505 (20°)	1.4648 (20°)	41.99
$(CH_3)_2NPO(OCH_3)_2$		77 to 78	1.1117 (20°)	1.4200 (20°)	34.86
$[(CH_3)_2N]_2PO(OCH_3)$		87 to 88	1.0647 (20°)	1.4385 (20°)	41.01
$(C_2H_5)_2NPO(OCH_3)_2$		90 to 91	1.0665 (20°)	1.4264 (20°)	43.57
$(C_2H_5)_2NPO(OC_2H_5)_2$		96 to 97	1.0115 (20°)	1.4240 (20°)	52.81
$(C_2H_5)_2NPO(Cl)CH_3$		109 to 110	1.1277 (20°)	1.4672 (20°)	41.75
$C_6H_5PSCl_2$		122 to 123	1.4050 (20°)	1.6230 (20°)	53.10
$(C_6H_5)_2PCl$		170 to 171	1.1801 (20°)	1.6340 (20°)	66.86
$C_6H_5OPOCl_2$		110 to 111	1.4160 (20°)	1.5231 (20°)	45.53
$4\ CH_3{\cdot}C_6H_4OPOCl_2$		124 to 125	1.3599 (20°)	1.5209 (20°)	50.38
$4(CH_3)_3C{\cdot}C_6H_4OPOCl_2$		147 to 148	1.2470 (20°)	1.5140 (20°)	64.48
$4\ Cl{\cdot}C_6H_4OPOCl_2$		134 to 135	1.5214 (20°)	1.5394 (20°)	50.57
$2,4\text{-}Cl_2{\cdot}C_6H_3OPOCl_2$		147 to 148	1.6088 (20°)	1.5580 (20°)	56.09
$2,4,5\text{-}Cl_3{\cdot}C_6H_2OPOCl_2$		167 to 168	1.6929 (20°)	1.5694 (20°)	60.87
$2,4,6\text{-}Cl_3{\cdot}C_6H_2OPS(Cl)(OCH_3)$	58 to 59		1.5410 (60°)	1.5569 (60°)	68.74
$2,4,5\text{-}Cl_3{\cdot}C_6H_2OPS(Cl)(OCH_3)$	38 to 39		1.5526 (40°)	1.5780 (40°)	68.73
$2,4,5\text{-}Cl_3{\cdot}C_6H_2OPS(Cl)(OC_2H_5)$	14 to 15		1.5202 (20°)	1.5760 (20°)	74.02
$2,4,5\text{-}Cl_3{\cdot}C_6H_2OPS(OCH_3)_2$	41		1.4575 (50°)	1.5530 (50°)	70.60
$H_2N{\cdot}NHPS(OCH_3)_2$			1.368 (25°)	1.5428 (25°)	35.96
$H_2N{\cdot}NHPS(OC_2H_5)_2$			1.185 (25°)	1.5010 (25°)	45.79

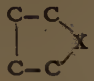
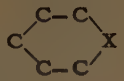
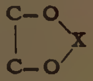
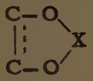
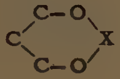
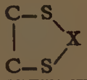
tures is caused by ring strain or electrophilic ring substitution and that optical depression may occur in the absence of these factors with saturated rings also. Thus, it is evident that both optical exaltation and depression are caused by electron shifts or changes in electron cloud density and that, consequently, they should be related to electron polarizability.

For a number of heterorings experimental values of refraction can be determined from available data of molar refraction of heterocyclic organophosphorus compounds by the method described in the preceding section. The refractive data obtainable in this manner are as given in TABLE 19 (GR values). They are remarkable for their lack of constancy. With these values determined from experimental data reported by Arbuzov, Kabachnik, Jones, and their respective co-workers (see bibliographical references in TABLE 19), there is little likelihood that inaccuracy of experimental source data could be the cause of lack of constancy. Most probably a fact, this nonconstancy of refraction of a given phosphorus-containing ring group requires theoretical explanation that may be developed in the following manner.

Substitution of carbon for phosphorus in the ring systems given in TABLE 19 produces groups whose data of refraction are as listed in column 2 of this table. The differences between these data and the refractive data of ring analogues containing phosphorus are listed in column 6. The magnitude of these differences can be determined also theoretically from known data given in TABLES 2, 3, 5, and 6, and has values as given in column 5 of TABLE 19. The discrepancies between the data of columns 5 and 6 can be explained in terms of optical depression and exaltation exhibited by the phosphorus-containing rings involved (see columns 7 and 8). According to this theory, the nature and amount of optical deviation shown by a given heteroring vary with the nature of the group attached to the ring by the $3s^2$ electrons and the third of the $3p^3$ electrons of phosphorus. While the influence of a group attached by the remaining $3p^3$ electron is rather small, it becomes quite marked with groups attached by the $3s^2$ electrons of phosphorus. This effect may be understood in terms of delocalization of the π-bond formed. Delocalization of such bonds is known to decrease optical depression and, sometimes, to convert it to exaltation.[118] The extent of optical deviation shown by a given heteroring remains constant, of course, for members of a homologous series of compounds containing the ring. These findings indicate that apparent anomalies in the refractive properties of heterocyclic organophosphorus compounds fit the previously mentioned general pattern of refractive behavior of other heterocyclic structures.

TABLE 19

REFRACTION OF PHOSPHORUS-CONTAINING RINGS (DATA IN CUBIC CENTIMETERS PER MOLE FOR *D*-LIGHT)

Ring structure	GR Values			Change of GR		Nature of GR change	
	X representing						
	Carbon*	Phosphorus	Ref.	Theor.	Actual	Depress.	Exaltat.
	2	3	4	5	6	7	8
	6.3	7.44	13	+ 1.1	+ 1.14		0.04
	7.62	8.29 to 8.73	13	+ 1.1	+ 0.67 to + 1.11	0.43	0.01
	7.3	6.52 to 7.12	60,119-122	− 0.34	− 0.78 to − 0.18	0.44	0.16
	8.73	7.63 to 8.63	37,39,121,124	− 0.34	− 1.1 to − 0.1	0.76	0.24
	8.58	7.57 to 8.57	60,119	− 0.34	− 1.01 to − 0.01	0.67	0.33
	19.7	19.98 to 20.48	60	+ 2.08	+ 0.28 to + 0.78	1.3 to 1.8	

*Data from Vogel *et al.*[8]

Parachor and Refrachor

On the basis of the data given in TABLES 13 to 17 it is possible to compute values of molar refraction of organophosphorus compounds belonging to more than one hundred different types of structure from a set of values of polarizability of electron groups involving valence electrons of phosphorus. It may be visualized that, if molar refraction represents an adequate quantitative characterization of a compound, it may be related to other additive as well as constitutive properties of the compound. Two properties of this kind are parachor $[P]$ and rheochor $[R]$, which were introduced by Sugden[125] and by Friend and Hargreaves.[126] In temperature regions of negligible vapor density of a given compound they are defined as follows (σ = surface tension, η = viscosity, d = liquid density):

$$[P] = \frac{M}{d} \cdot \sqrt[4]{\sigma} \qquad [R] = \frac{M}{d} \cdot \sqrt[8]{\eta} \tag{8}$$

All three molecular properties $[P]$, $[R]$, and molar refraction, R_D, are related to the molar volume, $\frac{M}{d}$ [127,128].

$$\frac{M}{d} = R_D \cdot \frac{n^2+2}{n^2-1} = \frac{[P]}{\sqrt[4]{\sigma}} = \frac{[R]}{\sqrt[8]{\eta}} \tag{9}$$

A more simple relationship between $[P]$ and R_D, however, is implicit in an equation established empirically by Samygin[129] (k' and k'' being constants characteristic of a given type of compound):

$$\sqrt[4]{\sigma} = k' \cdot \frac{n^2-1}{n^2+2} + k'' \cdot \frac{d}{M} \tag{10}$$

Multiplication of this equation with the molar volume directly results in the following straightforward relationship between $[P]$ and R_D:

$$[P] = k' \cdot R_D + k'' \tag{11}$$

As it is well known that the parachor, contrary to molar refraction, is affected by molecular association, EQUATION 11 must be changed to

$$[P] = a \cdot (k' \cdot R_D + k'') \tag{12}$$

In this equation, the factor a has a value of 1 if the compound involved is not associated, and a value of 2 or 3 if the compound is dimeric or trimeric, respectively. The constants k' and k'' can be determined graphically by plotting experimental parachor values against theoretical values of molar refraction. In this manner the data given for k' and k'' in TABLE 20 were obtained.

On the basis of EQUATION 12 and by means of the data of TABLE 20 it was possible to compute parachor data for various organophosphorus compounds and to compare them with known experimental data, as shown in TABLE 21. The results obtained indicate that both EQUATIONS 10 and 12 hold with phosphorus compounds, although Samygin's[129] relationship, that is, EQUATION 10 has been criticized as being not accurate for other types of organic compound.[130,131]

Rheochor. In view of the correlations expressed by EQUATION 9 it is likely that the rheochor also shows a simple relationship to molar refraction, possibly analogous to EQUATION 12. At present, sufficient experimental data of viscosity are not available for various types of organophosphorus compounds to prove relationship.

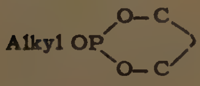
Refrachor. Several years ago, Joshi and Tuli[138] introduced the so-called refrachor $[F]$ as a molecular property that is characteristic of structure

$$[F] = -[P] \cdot \log (n_D^{20} - 1) \qquad (13)$$

The refrachor was found to be more suitable than the parachor for determination of keto and enol forms in tautomeric systems of carbonyl compounds.[138] In view of the existence of tautomeric forms of organophosphorus compounds it was of interest to determine refrachor data

TABLE 20

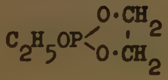
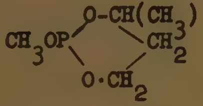
CONSTANTS k' AND k'' IN EQUATION 12

Type of compound	k'	k''
$(\text{Alkyl O})_3\text{P}$	8.35	26
	8.0	31
$(\text{Alkyl O})_3\text{PO}$	8.25	56
$(\text{Alkyl O})_3\text{PS}$	8.30	21
$\text{Alkyl SPS(O alkyl)}_2$	8.0	0
$\text{H}\cdot\text{PO (O alkyl)}_2$	8.3	41
$\text{Alkyl PO(O alkyl)}_2$	8.3	38
(Alkyl)(H)PO(O alkyl)	8.3	30
$\text{Cl}_2\text{P(O)R}^*$	8.2	28.5
$\text{ClP(O)(R)}_2{}^*$	8.2	43.0
$\text{FP(O)(R)}_2{}^*$	8.2	54.5

*R representing O-alkyl or N(alkyl)_2.

TABLE 21

THEORETICAL AND EXPERIMENTAL PARACHOR VALUES

Compound	[P]		
	Calc.	Obs.	Ref.
$(CH_3O)_3P$	268.4	267.5	56
$(C_2H_5O)_3P$	384.9	381.9	56
$(C_3H_7O)_3P$	501.2	496.1	56
$(C_4H_9O)_3P$	616.9	619.6	56
$(C_6H_{13}O)_3P$	850.6	853.5	132
$(C_8H_{17}O)_3P$	1083.5	1084.1	132
	282.4	281.4	133
	319.6	319.6	133
$(CH_3O)_3PO$	285.2	286.2	77,134
$(C_2H_5O)_3PO$	400.3	399, 400	77,134
$C_2H_5P(O)(H)OC_2H_5$	282.3	282.0	135
$C_2H_5P(O)(H)OC_6H_{13}$	436.6	436.5	135
$C_2H_5P(O)(H)OC_9H_{19}$	552.4	553.7	135
$CH_3PO(OCH_3)_2$	260.3	260.1	56
$CH_3PO(OC_8H_{17})_2$	800.5	802.5	61
$C_2H_5PO(OC_2H_5)_2$	376.1	375.5	56
$C_3H_7PO(OC_3H_7)_2$	491.8	490.12	56
$C_4H_9PO(OC_4H_9)_2$	607.6	608.1	56
$C_{10}H_{21}PO(OC_{10}H_{21})_2$	1301.9	1310.8	61
$(CH_3O)_2PHO$	449	452.7	136
$(C_2H_5O)_2PHO$	603.2	605.3	136
$(C_3H_7O)_2PHO$	757.6	758	136

$(C_3H_7O)_3PO$	515.3	516	77,134	$(C_4H_9O)_2PHO$	911.8	909.4	136
$(C_4H_9O)_3PO$	630.4	627-631	77,134	$(C_6H_{13}O)_2PHO$	1220.4	1216	136
$(C_6H_{13}O)_3PO$	860.4	857.2	132	$(C_7H_{15}O)_2PHO$	1374.8	1372	136
$(ClC_2H_4O)_3PO$	519.9	515.2	75	$(C_8H_{17}O)_2PHO$	1529.2	1525	136
$(C_2H_5O)_3PS$	431.3	431.2	56	$(C_2H_5O)_2POCl$	339.4	339	137
$(C_3H_7O)_3PS$	546.7	545.4	132	$(C_3H_7O)_2POCl$	415.7	419.9	137
$(C_4H_9O)_3PS$	662.8	660.2	132	$(C_2H_5O)PO(Cl)N(CH_3)_2$	355.6	351.1	137
$(C_6H_{13}O)_3PS$	894.2	892.6	132	$(C_2H_5O)_2POF$	306.2	307.6	137
$(C_8H_{17}O)_3PS$	1125.7	1126.4	132	$(C_3H_7O)_2POF$	382.5	387.3	137
$(CH_3O)_2PS(SCH_3)$	343.1	343.7	87	$[(CH_3)_2N]_2POF$	338.5	332.3	137
$(C_2H_5O)_2PS(SH)$	383.6	379.3	87	CH_3OPOCl_2	241.1	242.5	137
$(C_2H_5O)_2PS(SC_2H_5)$	454.7	460.4	87	$C_2H_5OPOCl_2$	279.3	282.3	137
$(C_3H_7O)_2PS(SC_3H_7)$	566.2	565.6	87	$(CH_3)_2NPOCl_2$	295.4	291.3	137
				$(C_2H_5)_2NPOCl_2$	371.6	370.7	137

experimentally for various types of organophosphorus compound; the data obtained were as given in TABLE 22. As to be expected from EQUATION 12, the refrachor data were found to be related to data of molar refraction according to the equation (K' and K'' being constants characteristic of a given type of compound)

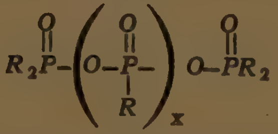
$$[F] = K' \cdot R_D + K'' \qquad (14)$$

A comparison of values of R_D, $[P]$, and $[F]$ of components present in certain tautomeric systems of phosphorus compounds showed that refractive data are relatively most suitable for determination of components.

Other Molecular Data

Refractive index. Many years ago Eisenlohr[139] discovered that the product of molecular weight and refractive index, $M \cdot n_D^{20}$, showed a remarkable degree of additivity for various types of organic compound. Eisenlohr suggested that this product, which he called molecular refraction "coefficient", be substituted for the Lorentz-Lorenz expression of molar refraction because of its apparently stricter additivity. Subsequently, a sufficient number of theoretical values of atomic and bond increments became available for calculation of data for Eisenlohr's "coefficient" of a given organic compound.[8,12,25] Division of molecular weight values into theoretical data of this "coefficient" should produce values nearly identical to the experimental refractive indices of the compounds involved. An investigation of various types of organophosphorus compound showed that values of refractive indices, when determined in this manner, did not show sufficiently favorable agreement with experimental data to attach practical importance to this possibility.

Molecular weight. Among organic polyphosphorus compounds the following family of compounds is known (R representing a dimethylamido group[106]):



$$R_2\overset{O}{\overset{\|}{P}}-\left(O-\underset{R}{\underset{|}{\overset{O}{\overset{\|}{P}}}}-\right)_x O-\overset{O}{\overset{\|}{P}}R_2 \qquad (15)$$

From theoretical data of molar refraction and experimental data of refractive index and density it should be possible to determine the molecular weight of various members of this family of compounds. Theoretically, the molar refractions and molecular weights of these compounds are given by the relationships $R_D = 69.18 + 21.55 \cdot x$ and, $M = 286.25 + 107.05 \cdot x$. Introduction of these expressions into the Lorentz-Lorenz equation, elimination of x, and reintroduction of the

TABLE 22

MOLAR REFRACHOR [F] OF ALIPHATIC P-COMPOUNDS

Structure	Alkyl group				K'	K''
	CH_3	C_2H_5	C_3H_7	C_4H_9		
$(\text{Alkyl O})_3P$	107.5	160.4	212.83	266.13	3.69	
$(\text{Alkyl O})_3PO$	109.2	162.12	214.61	267.93	3.88	
$(\text{Alkyl O})_3PS$	140.71	193.81	246.75	300.0	3.92	
$\text{Alkyl SPS(O alkyl)}_2$	181.89	235.3	288.74		3.90	13.5
(Alkyl)(H)PO(O alkyl)		119.63			3.93	
ClPO(O alkyl)_2		141.73	175.3		3.88	
FPO(O alkyl)_2		114.2	148.1		3.72	
$\text{Cl}_2\text{PO(O alkyl)}$		105.1	122.7		3.85	5.3
$\text{Cl}_2\text{PO[N(alkyl)}_2]$		135.1	172.0		4.14	
$\text{Alkyl PO(O alkyl)}_2$	103.4	156.32	208.81	262.13	3.84	

expression obtained for x into the molecular weight expression results in the equation (if $n^2-1/n^2+2 = L$)

$$M = 286.25 + 343.65 \cdot \frac{d-4.138 \cdot L}{4.968 \cdot L-d} \qquad (16)$$

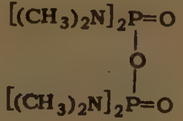
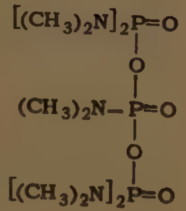
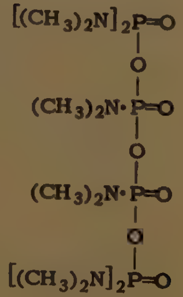
Determination of molecular weights on the basis of EQUATION 16 was found to be as accurate as cryoscopic determination, as shown in TABLE 23. Obviously, this method of molecular weight determination should be applicable to other families of organic compounds, also, after proper modification of EQUATION 16.

POLARIZATION AND EQUILIBRIUM PHENOMENA

According to the relationship expressed by EQUATION 5, changes in induced polarization and in free energy of a given chemical system should be quantitatively correlated. Inasmuch as the actual position of an equilibrium and the degree of probability of a given rearrangement or reaction are controlled by changes in free energy, they should be reflected in changes of induced polarization also. It was of interest, therefore, to compare changes in polarizability with experimentally

TABLE 23

MOLECULAR WEIGHTS ACCORDING TO EQUATION 16

Compound		A	B	C	D	E
d_4^{t}*		1.0253 (20°)	1.1360 (25°)	1.1931 (20°)	1.1938 (20°)	1.2561 (20°)
n_D^{t}*		1.4582 (20°)	1.4620 (25°)	1.4644 (20°)	1.4639 (20°)	1.4719 (20°)
M	EQUAT. 16	178	284	383	388	535
	cryoscop.*		288	405	409	510
	theor.	179.2	286.3	393.3		500.4
Actual structure		$[(CH_3)_2N]_3PO$	 $[(CH_3)_2N]_2P{=}O-O-[(CH_3)_2N]_2P{=}O$	 $[(CH_3)_2N]_2P{=}O-O-(CH_3)_2N{-}P{=}O-O-[(CH_3)_2N]_2P{=}O$		 $[(CH_3)_2N]_2P{=}O-O-(CH_3)_2N{\cdot}P{=}O-O-(CH_3)_2N{\cdot}P{=}O-O-[(CH_3)_2N]_2P{=}O$

* Experimental data from Tolkmith.[106]

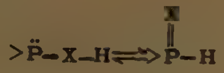
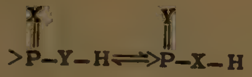
obtained information on tautomeric systems, intramolecular rearrangements, addition reactions, and decomposition reactions involving organophosphorus compounds. Changes in polarizability could be expressed quantitatively as differences in theoretical values of molar induced polarization $\Delta[a_t]$.

In a series of tautomeric systems a shift from one component to the other shows a certain decrease in polarizability (see TABLE 24). This decrease is substantial in the case of systems 1*a*, 1*b*, and 2*a*, moderate in the case of system 3*a*, and negligible for systems 4*a* and 4*b*. Experimental investigation has shown that the systems 1*a*, 1*b*, and 2*a* contain the less polarizable tautomer almost exclusively.[28,92,140] System 3*a* has been found to contain both components in more or less substantial amounts,[45] while equilibrium 4*a* in solution has been reported to depend upon the nature of the solvent employed.[18] From these findings it may be concluded that the conversion of the group $H{-}X{-}\ddot{P}{<}$ to the group $H{-}\overset{|}{\underset{|}{P}}{=}X$ causes a marked decrease in free energy, while the conversion of $>P(Y)(XH)$ to $>P(X)(YH)$ shows practically no change in free energy. This appears understandable on theoretical grounds. In the first case two σ-bonds are changed to a different σ-bond plus a $\sigma\pi$-bond. In the second case there is no difference in the number of bonds, while differences in the nature of the bonds in either tautomer appear to be compensated. Hence, no source causing a notable change in free energy is evident. However, one investigation[91] has shown a predominance of thiono tautomer in system 4*b*.

Intramoleuclar rearrangements show the following relationships between polarizability and change in free energy (compare TABLE 25). Various modifications of the well-known Michaelis-Arbuzov rearrangement involve reaction products that are considerably less polarizable and have less free energy than the isomeric starting products. Reconversion of such compounds into their starting products thus appears to be improbable. Experimental investigation has shown that in the case of the systems 5*a*,[36,141-143] 5*b*,[143,144] 6*a*,[143,144] and 6*b*[145] the less polarizable component could not be reconverted to its isomeric form. Rearrangements according to system 7*a* have been discovered by Forbes and Anderson;[146,147] information as to possible reversibility of this system is not available at the present time. The systems 8*a* and 8*b* are somewhat similar to the equilibria 4*a* and 4*b*, although the thiolo form of system 8*a* is noticeably less polarizable than the isomeric thiono form. This fact explains, at least qualitatively, the unexpected formation of the thiolo form[94] from O,O-dialkyl sodiumphosphorothioates that are known to exist in thiono configuration only.[91,94] The isomeric pyrophosphates of system 8*b* have practically the same data of polarizability. Therefore, their structure should depend upon the nature of

TABLE 24

TAUTOMERIC EQUILIBRIA

Type	No.	System	$\Delta[a_l]$*
 $>\ddot{P}-X-H \rightleftharpoons >\overset{X}{\overset{\|}{P}}-H$	1a	$(\text{Alkyl O})_2\ddot{P}(\text{OH}) \longrightarrow (\text{Alkyl O})_2P(\text{O})(\text{H})$	− 2.3
	1b	Phenyl $\ddot{P}(\text{O alkyl})(\text{OH}) \longrightarrow$ phenyl $P(\text{O})(\text{H})(\text{O alkyl})$	− 2.3
	2a	$(\text{Alkyl O})_2\ddot{P}(\text{SH}) \longrightarrow (\text{Alkyl O})_2P(\text{S})(\text{H})$	− 2.35
	3a	$(\text{Alkyl O})_2\ddot{P}(\text{NH phenyl}) \longrightarrow (\text{Alkyl O})_2P(\text{H})(\text{N phenyl})$	− 0.66
 $>\overset{X}{\overset{\|}{P}}-Y-H \rightleftharpoons >\overset{Y}{\overset{\|}{P}}-X-H$	4a	$(\text{Alkyl O})_2P(\text{O})(\text{SH}) \longrightarrow (\text{Alkyl O})_2P(\text{S})(\text{OH})$	− 0.05
	4b	$(\text{Alkyl O})(\text{Alkyl})P(\text{O})(\text{SH}) \longrightarrow (\text{Alkyl O})(\text{Alkyl})P(\text{S})(\text{OH})$	− 0.05

* Theoretical values in cubic centimeters per mole.

TABLE 25

INTRAMOLECULAR REARRANGEMENTS

Type	No.	System	$\Delta[a_i]$†
$>\ddot{P}(O/S\ Alkyl) \rightleftarrows >\overset{O/S}{\overset{\parallel}{P}}(Alkyl)$	5a*	$(R')_2\ddot{P}(O\ alkyl) \longrightarrow Alkyl\ P(O)(R')_2$	−2.25
	5b	$(Phenyl)_2\ddot{P}(O\ alkyl) \longrightarrow (Phenyl)_2P(O)(Alkyl)$	−2.25
	6a	$(Phenyl)_2\ddot{P}(S\ alkyl) \longrightarrow (Phenyl)_2P(S)(Alkyl)$	−1.91
	6b	$Phenyl\ \ddot{P}(S\ alkyl)_2 \longrightarrow (Phenyl)(Alkyl)P(S)(S\ Alkyl)$	−1.91
	7a	$>P-N=C=O \longrightarrow >P-O-C\equiv N$	−1.3
$>\overset{S}{\overset{\parallel}{P}}-O \rightleftarrows >\overset{O}{\overset{\parallel}{P}}-S$	8a	$(Alkyl\ O)_3PS \longrightarrow (Alkyl\ O)_2P(O)(S\ Alkyl)$	−0.34
	8b	$(Alkyl\ O)_2P(S)\cdot O\cdot P(O)(O\ Alkyl)_2 \longrightarrow [(Alkyl\ O)_2P(O)]_2S$	−0.05

* R′ representing O-alkyl or N(alkyl)$_2$.

† Compare TABLE 24.

the solvent and the reaction temperature, as employed in their preparation: Fiszer *et al.*[115] have found that the thiolo configuration of system 8*b* is formed in ether below 35° C., while Schrader and Muhlmann[148] have obtained the thiono isomer in water above 35° C.

Definite relationships between change in induced polarization and change in free energy are also evident in certain addition reactions and decomposition reactions (see TABLE 26). According to the amount of change in polarizability, the formation of reaction products 9*a* and 10*a* is less probable than the formation of the products 9*b* and 10*b*. Experimental investigation has shown that the compounds actually produced had the structures 9*b*[149] and 10*b*.[150] Reversibility of reaction, as indicated by unchanged polarizability $\Delta[\alpha_i]=0$, has been established experimentally for the systems 11*a*,[151] 12*a*,[106,152] 13*a*,[153] 17*a*,[154] and 18*a*.[106]

An interesting situation exists with some decomposition reactions, such as 14*a*, 14*b*, 15*a*, 15*b*, 16*a*, and 16*b*. The main products formed could be either monomeric or polymeric. Monomeric configuration appears quite unlikely as it would result not only in a great increase in polarizability, but also in the formation of two $\sigma\pi$-bonds at the same phosphorus atom. Consequently, the reaction products should have polymeric structure. Experimental investigation has shown that the main products were dimers of cyclic structure.[155-157]

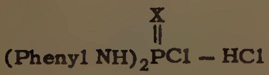
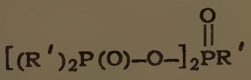
The findings reported disclose the existence of a proportionality between changes in polarizability and changes in free energy of reaction systems involving organophosphorus compounds. This relationship bears similarity to the relationship between polarity and heat of combustion of carbon compounds, as discovered by Kharasch and Sher.[158]

SUMMARY AND CONCLUSION

The aim of the investigation described was an elucidation of quantitative relationships between the state of the valence electrons of phosphorus and various molecular properties of organophosphorus compounds. The investigation was based upon the concept of electron-group polarizability as a characteristic of valence electrons. The $3s^2 3p^3$ electrons of phosphorus were quantitatively characterized by data of mean induced polarizability of electron groups containing one of the $3p^3$ electrons and, respectively, both of $3s^2$ electrons of phosphorus. The polarizability data were determined in Å^3 units from known data of refraction according to the familiar relation $\alpha_i = \alpha_A + \alpha_E = 3R_D/4\pi N$. On the basis of the concept employed it was also possible to determine data of mean polarizability for unshared electron pairs themselves, that is, for the $3s^2$ electrons on phosphorus and the $2s^2$ electrons on

TABLE 26

ADDITION REACTIONS AND DECOMPOSITION REACTIONS

System[*]	No.	Reaction products	$\Delta[a_i]$[†]
$(\text{Alkyl})_2\text{CO} + \text{HPO(OH)}_2$	9*a*	$(\text{Alkyl})_2\text{CH}\cdot\text{O}\cdot\text{PO(OH)}_2$	− 1.0
	9*b*	$(\text{Alkyl})_2\text{C(OH)PO(OH)}_2$	− 2.0
$\text{Alkyl CH{=}CH}_2 + \text{PCl}_3$	10*a*	$\text{Alkyl CH{=}CHPCl}_2 + \text{HCl}$	− 0.1
	10*b*	$\text{Alkyl CHClCH}_2\text{PCl}_2$	− 1.46
$2\,(\text{Phenyl O})_3\text{P} + \text{PCl}_3$	11*a*	$3\,(\text{Phenyl O})_2\text{PCl}$	0
$n(\text{R}')_3\text{PO} + (\text{R}'\text{PO}_2)_n$	12*a*	$n[(\text{R}')_2\text{P(O)}]_2\text{O}$	0
$n(\text{Alkyl S})_3\text{PS} + (\text{P}_2\text{S}_5)_n$	13*a*	$3\,(\text{Alkyl SPS}_2)_n$	0
$(\text{Phenyl NH})_3\text{P{=}X} - \text{phenyl NH}_2$	14*a*	$\text{Phenyl NHP(X){=}N phenyl}$	+ 2.42
	14*b*	$1/n\,(\text{Phenyl NH}\underset{\mid}{\text{P}}\text{(X)}-\underset{\mid}{\text{N}}\text{ phenyl})_n$	− 0.38
 $(\text{Phenyl NH})_2\overset{\overset{\text{X}}{\parallel}}{\text{P}}\text{Cl} - \text{HCl}$	15*a*	$\text{Phenyl NHP(X){=}N phenyl}$	+ 2.42
	15*b*	$1/n\,(\text{Phenyl NH}\underset{\mid}{\text{P}}\text{(X)}-\underset{\mid}{\text{N}}\text{ phenyl})_n$	− 0.38
$\text{Phenyl NH}\overset{\overset{\text{X}}{\parallel}}{\text{P}}\text{Cl}_2\text{—HCl}$	16*a*	$\text{ClP(X){=}N phenyl}$	+ 2.24
	16*b*	$1/n\,(\text{Cl}\underset{\mid}{\text{P}}\text{(X)}-\underset{\mid}{\text{N}}\text{ phenyl})_n$	− 0.56
$2\ \text{Phenyl PCl}_2\text{—PCl}_3$	17*a*	$(\text{Phenyl})_2\text{PCl}$	0
$2[(\text{R}')_2\text{P(O)}]_2\text{O—(R}')_3\text{PO}$	18*a*	 $[(\text{R}')_2\text{P(O)—O—}]_2\overset{\overset{\text{O}}{\parallel}}{\text{P}}\text{R}'$	0

[*] R′ being O—alkyl or N(alkyl)_2, and X representing oxygen or sulfur.

[†] Compare TABLE 24.

nitrogen. With the establishment of data that quantitatively characterize electron groups containing valence electrons of phosphorus, it was possible to investigate relationships between these data and various molecular properties of compounds containing either 3 or 4 atoms directly attached to phosphorus. The following results were obtained.

Bond data. A mathematical relation between mean polarizability of electron groups, containing one of the $3p^3$ electrons of phosphorus, and bond energy as well as interatomic distance was empirically established. Increments of refraction pertaining to various phosphorus bonds were determined. They were found to be constant and independent of structure only in those cases that involved attachment of a univalent atom to phosphorus (P–H, P–Halogen). Refractive increments pertaining to σ-bonds between phosphorus and, respectively, carbon, nitrogen, oxygen, and sulfur were found to vary characteristically with structure, as was to be expected from the viewpoint of the electronic theory of structure. Refractive increments of $\sigma\pi$-bonds between phosphorus and bivalent atoms, such as oxygen and sulfur ($P \rightarrow O$, $P \rightarrow S$), were found to be constant and independent of structure, as was to be expected theoretically. Apparently negative values of refractive increment, as reported for the coordinate-covalent $P \rightarrow O$ bond, were found to result from calculations based upon valence-bond structures. The inadequacy of such structures for investigations involving refraction was first pointed out by Fajans,[1] as well as by Smyth.[2]

Molecular data. Data of molar refraction, when calculated theoretically as the sum of data of mean induced polarizability, were found to be in satisfactory agreement with experimental data of more than 500 organophosphorus compounds. Experimental data of parachor and refrachor also were found to fit a simple mathematical relation with molar, induced polarization. It was concluded from the existence of these relationships that molar refraction, parachor, and refrachor are quantitative expressions of molar, induced polarization. This explains the constitutive and essentially additive nature of these molecular properties.

The group refraction of phosphorus-containing heterocyclic rings was not found to be independent of structure but to show optical depression, which varies somewhat if the $3s^2$ electrons of phosphorus are engaged in formation of $\sigma\pi$-bonds. In this case optical depression appears to be associated with π-bond delocalization.

Free energy. A study of tautomeric equilibria, intramolecular rearrangements, and certain addition reactions, as well as decomposition reactions, disclosed that changes in molar, induced polarization and changes in free energy apparently are directly proportional.

Conclusion. The quantitative relations established between chemical structure and some properties of organophosphorus compounds apparently represent a first, though incomplete, system for this class of compound. Within the limits of its applicability it may contribute to the elevation of organic phosphorus chemistry to a less empirical level.

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